

# Impeding $^{99}\text{Tc(IV)}$ mobility in novel waste forms

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## Abstract

Techetium ( $^{99}\text{Tc}$ ) is an abundant, long-lived radioactive fission product whose mobility in the subsurface is largely governed by its oxidation state. Tc-immobilization is crucial for radioactive waste management and environmental remediation. Tc(IV) incorporation in spinels has been proposed as a novel method to increase Tc retention in glass waste forms during vitrification. However, experiments under high temperature and oxic conditions show reoxidation of Tc(IV) to volatile pertechnetate, Tc(VII). Here, we examine this problem with *ab initio* molecular dynamics simulations and propose that at elevated temperatures, doping with 1<sup>st</sup> row transition metal can significantly enhance Tc retention in magnetite in the order Co > Zn > Ni. Experiments with doped spinels at 700 °C provide quantitative confirmation of the theoretical predictions in the same order. This work highlights the power of modern, state-of-the-art simulations to provide essential insights and generate theory-inspired design criteria of complex materials at elevated temperatures.

## 1 Introduction

2 Technetium ( $^{99}\text{Tc}$ ) is an abundant long-lived radioactive fission product present in  
3 used nuclear fuel and waste generated from nuclear fuel reprocessing. Due to its  
4 long half-life ( $2.1 \times 10^5$  y) and relatively high fission yield ( $\sim 6\%$ ),  $^{99}\text{Tc}$  can generate  
5 the greatest radiation dose in the vicinity of a waste repository, and for a much  
6 longer time compared with other fission products, such as  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  (with half-  
7 life  $\sim 30$  years).<sup>1, 2</sup> In addition,  $\text{TcO}_4^-$  is highly soluble and weakly adsorbed in the  
8 near-field, while  $\text{Tc(IV)}$  is highly adsorbable to geological materials and clays.<sup>3</sup> Thus,  
9 migration of Tc from a waste repository may be prevented by immobilizing  $\text{Tc(IV)}$   
10 in durable waste forms, such as glass or ceramic materials.<sup>4-6</sup> Although  $\text{Tc(VII)O}_4^-$  is  
11 the most stable Tc species under aerobic conditions, it is highly volatile at glass  
12 vitrification temperatures ( $\sim 1,200$  °C) leading to poor Tc retention in the final waste  
13 glass.<sup>4-7</sup> Retention of Tc in the glass is generally improved by reducing conditions  
14 since  $\text{Tc(IV)}$  is less volatile.<sup>6, 8, 9</sup>  $\text{Tc(VII)}$  may be effectively reduced to  $\text{Tc(IV)}$  by  
15  $\text{Fe(II)}$  in oxide and sulfide minerals or by  $\text{Fe(II)}$  adsorbed to mineral surfaces such  
16 as iron oxides or aluminum oxides.<sup>9-17</sup> However, retention of Tc is still limited due to  
17 reoxidation of  $\text{Tc(IV)}$  back to  $\text{Tc(VII)}$ .<sup>18-21</sup> Consequently, simply reducing  $\text{Tc(VII)}$  to  
18  $\text{Tc(IV)}$  prior to vitrification is unlikely to stabilize Tc and prevent its volatilization as  
19  $\text{Tc(VII)}$ . An alternative approach would be to trap  $\text{Tc(IV)}$  in the lattice of a metal  
20 oxide by co-precipitation. Spinel is attractive targets for Tc stabilization during  
21 vitrification because of their physical and chemical stability under the high  
22 temperatures used in preparing borosilicate glasses.<sup>4, 6</sup> In this respect, efficient

1 incorporation and high retention of Tc by glass-incorporated spinels is very  
2 important for radioactive waste management and offers substantial economic  
3 benefit due to reduction in the amount of glass needed to immobilize  $^{99}\text{Tc}$ .

4 Magnetite ( $\text{Fe}_3\text{O}_4$ ) has a cubic inverse spinel structure, where the oxygen  
5 anions form a slightly distorted face-centered-cubic (fcc) sublattice and the iron  
6 cations occupy tetrahedral and octahedral interstitial sites. In the [001] direction,  
7 two types of layer stacking occur: *A* layers with tetrahedral Fe(III) and *B* layers with  
8 O and octahedral Fe(II)/Fe(III), see Figure 1. Marshall *et al.* showed that Tc(VII) can  
9 reduced to Tc(IV) and incorporated into the magnetite structure under high pH  
10 conditions (pH 10.5–13.1).<sup>8</sup> They also observed that Tc(IV) incorporation occurred  
11 at the octahedral sites and remobilization of Tc(IV) was limited during subsequent  
12 air oxidation. However, magnetite oxidizes to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) in oxic  
13 conditions or under high temperature through maghemitization, where all the Fe(II)  
14 atoms oxidize to Fe(III), while the oxygen sublattice remains unchanged.<sup>22</sup> When  
15 maghematization takes place, iron atoms diffuse towards the surface, leaving  
16 octahedral cation vacancies.<sup>22,23</sup> As a result, maghematization could lead to  
17 reoxidation of Tc(IV) due to the increase in Fe(III), a highly efficient oxidizing  
18 agent.<sup>8</sup> Sidhu *et al.* suggested that incorporation of trace elements into magnetite  
19 stabilizes Fe(II) and suppresses maghematization by decreasing electron mobility.<sup>22</sup>  
20 The majority of experimental studies on Tc retention are conducted at low  
21 temperatures, while theoretical studies employ static structural models that neglect  
22 temperature effects. Under these conditions, these studies cannot address Tc  
23 volatilization during vitrification that leads to poor Tc retention in the glass waste

form. Thus, elucidation of high-temperature effects is important for understanding Tc retention by magnetite at elevated temperatures. *Ab initio* molecular dynamics (AIMD) simulations can describe the temperature effects on the change in structure, bonding and associated change in the oxidation states of Tc and Fe, which ultimately affects Tc retention. Our simulations indeed show that leaching of Tc is accompanied with re-oxidation of Tc(IV) to Tc(VII) at high temperatures, but it can be suppressed by doping. We propose that inclusion of 1<sup>st</sup> transition metal dopants (Co, Zn, Ni) significantly improves Tc retention in magnetite. Quantitative confirmation is further provided by XANES measurements and gravimetric analysis.

## Results

### Temperature effects on Tc(IV) incorporated spinel

The Fe<sub>3</sub>O<sub>4</sub>(001) surface has been studied extensively.<sup>24-29</sup> Pentcheva *et al.* compiled a phase diagram for the Fe<sub>3</sub>O<sub>4</sub>(001) surface in an *ab initio* thermodynamics study showing that the most stable surface structure is a *B*-terminated surface with octahedral iron and oxygen atoms forming a wavelike structure along the (001) direction.<sup>27</sup> Based on these results, we generated a Fe<sub>3</sub>O<sub>4</sub>(001) model of a *B*-terminated surface (Fig. 1) that we let fully relax. Below the Verwey transition (125 K), the surface possesses a permanent dipole, that has been shown to drive the formation of surface defects in these types of material.<sup>24</sup> However, above this temperature, magnetite is metallic and the surface dipole is quenched<sup>30</sup> and it is not likely to affect surface charge defects. Details on the computational models and methods can be found in the Methods section.

1        To assess the temperature effects on Tc retention in magnetite, we replaced  
2        one octahedral Fe on the surface with Tc and performed AIMD simulations at two  
3        different temperatures, 25 and 600 °C, representing the ambient and the lower-end  
4        temperature range of the vitrification process, respectively. Figure 2a shows the  
5        calculated atomic density profiles of the different species with Tc scaled by 5, for  
6        clarity. The dotted gray line denotes the edge of the magnetite surface defined by  
7        the average position of the topmost oxygen atoms. At 25 °C, Tc stays within the top  
8        surface layer for the duration of the simulation (~20 ps). Computation of pair  
9        distribution functions,  $g(R)$ , reveals that on average, surface-incorporated Tc has  
10       five nearest O neighbors with an average Tc-O distance 1.98 Å (Fig. 2b upper panel,  
11       Supplementary Fig. 1 and Supplementary Table 1). Additional exploratory  
12       simulations with Tc in an inner lattice position, shows a  $g(R)$  maximum at 2.01 Å for  
13       the Tc-O distance, compatible with the reduced Tc(IV) in magnetite, see  
14       Supplementary Table 2. According to X-ray absorption fine structure (XAFS)  
15       analysis, the Tc(IV)-O distance is ~2.0 Å, see Supplementary Table 2 and Ref. 31 for  
16       additional structural parameters. These observations imply that: (i) within the  
17       surface layer the oxidation state of Tc is essentially Tc(IV), and (ii) at 25 °C (the  
18       glass feed stage) reduced Tc(IV) is the prevalent oxidation state. However, the  
19       completely opposite picture emerges at high temperatures, 600 °C or higher. Tc  
20       moves above the surface, dragging coordinating surface oxygens along with it (see  
21       Supplementary Movie 1). The local Tc geometry is consistent with a tetrahedral  
22       Tc(VII)O<sub>4</sub><sup>-</sup> species, with two or three of the coordinating oxygens dynamically  
23       connected to Fe atoms on the surface (Fig. 2c). Analysis of  $g(R)$  for Tc-O pairs shows

1 a peak at 1.79 Å (Fig. 2b lower panel), an almost 10 % reduction compared to the  
2 Tc(IV)–O distance at 25 °C. This change is compatible with the shorter Tc(VII)–O  
3 distances of ~1.75 Å as determined by XAFS, Supplementary Table 2 and Ref. 32.  
4 From this observation, we infer that beginning at 600 °C, the Tc oxidation is in  
5 process, commensurate with the tetrahedrally coordinated Tc as it transitions to  
6 TcO<sub>4</sub><sup>-</sup>. In addition to the system with Tc at the surface, we also examined a system  
7 with Tc at an inner lattice site at 600 °C. The calculated  $g(R)$  gives the distance  
8 between Tc and O as 2.01 Å, consistent with the reduced Tc(IV) in magnetite. As  
9 shown in Supplementary Fig. 2, Tc remains in the same layer throughout the  
10 simulation timescale. When comparing the energetics of the configurations with Tc  
11 below or at the surface layer, the energy with Tc below the surface is 2.5 eV higher  
12 than when Tc is at the surface. This implies that there is a thermodynamic driving  
13 force that will eventually move Tc out to the surface.

14 Experimentally, Tc-magnetite samples heated from room temperature to 600  
15 °C then cooled back to room temperature were analyzed to determine the Tc  
16 oxidation state using X-ray absorption near edge structure (XANES) as shown in Fig.  
17 2d. In the figure, the grey diamonds and black line indicate the measured data and a  
18 linear combination fit, respectively, for Tc-magnetite samples, while the red and  
19 blue lines represent the contribution from Tc(IV) and Tc(VII), respectively. At 25 °C,  
20 the spectrum of the sample shows only Tc(IV) (feed, red) but no Tc(VII) (blue),  
21 indicating that all Tc in the sample is in its reduced form. In the sample heated to  
22 600 °C, however, the spectrum shows a mixture of both Tc(IV) and Tc(VII). All these  
23 observations are compatible with the simulations.

## 1 Effects of dopants on Tc retention

2 To simulate the effect of dopants on the Tc redox chemistry and immobilization, we  
3 modified the magnetite by substituting one surface Fe atom with Ni, Zn, or Co (~1 %  
4 wt each) at a site close to Tc. This choice was motivated by earlier experiments by  
5 Sidhu *et al.*, who observed stabilization of Fe(II) and suppression of  
6 maghematization when first row transition metal dopants were present in  
7 magnetite even at concentrations ~1 wt %.<sup>22</sup> The atomic density profiles along the  
8 surface normal from AIMD at 600 °C in the presence of the doping elements are  
9 shown in Fig. 3 (Co) and Supplementary Fig. 3 (Ni, Zn), exhibiting an increase of Tc  
10 retention in the order Co > Zn > Ni.

11 In the case of Ni, the Tc population is bi-modal where Tc remains mostly on  
12 top of the surface with only a small population within the top surface layer. In the  
13 case of Zn, the bi-modal Tc distribution is shifted towards a larger Tc population  
14 within the surface. Analysis of trajectories also shows that the distance between Tc  
15 and the coordinating O fluctuates between 1.71 and 1.92 Å, compatible with an  
16 equilibrium between Tc(VII) and Tc(IV) oxidation states (see Supplementary Fig.  
17 4). This behavior implies that Ni and Zn only partially, and to a similar degree,  
18 hinder Tc oxidation. Finally, in the presence of Co, Tc remains almost in its entirety  
19 within the surface at all times indicative of a Tc(IV) state. We examined Tc(IV)  
20 stabilization in the presence of Co by conducting a simulation starting with  $\text{TcO}_4^-$  on  
21 top of the surface. As shown in Supplementary Movie 2, Tc(VII) rapidly migrates  
22 into the surface becoming Tc(IV), within 1.5 ps of simulation time.

To validate these findings, we prepared three different magnetite samples doped with ~10 % wt of Ni, Zn and Co. Details on the preparation of samples can be found in the Experimental Methods section. The samples were heated at 700 °C in a furnace for one hour, and the remaining Tc was measured (see Supplementary Table 3). Gravimetric measurement showed that doping with Co resulted in the highest Tc retention (29 % wt) compared to less than half that amount for Zn (12 % wt) and about 1/8 of that for Ni (4 % wt). No detectable amount of Tc was found in the Tc-magnetite sample prepared without dopant and treated at 700 °C. We also performed XANES measurements for the samples prepared at 25 and 700 °C, see Supplementary Methods for details, and confirmed our theoretical prediction of the highest Tc retention with Co dopant at high temperature, as shown in Supplementary Table 4 and Fig. 3b and Supplementary Fig. 5.

### Equilibrium constants and free energy estimates

To best connect with the experimental observations, we determined the ratio of the equilibrium populations between the two different oxidation states of Tc(IV) ([Tc<sub>in</sub>]) and Tc(VII) ([Tc<sub>out</sub>]). This can be achieved by integrating the area under the atomic density profiles for Tc in Fig. 3. An equilibrium constant between the two populations, determined as the ratio  $K_{eq} = [Tc_{in}]/[Tc_{out}]$ , was used to calculate the Gibbs free energy for this equilibrium from the relation  $\Delta G = -RT \ln K_{eq}$ , where  $R$  is the gas constant and  $T$  is the absolute temperature. Negative values indicate that the equilibrium favors a higher population of Tc(IV). Table 1 summarizes the computed values of  $K_{eq}$  and  $\Delta G$ , as well as the measured Tc retention for the different doping

agents Ni, Zn, and Co. These results show a remarkable agreement between the theoretical prediction and experimental validations, not only in terms of relative order, but also in magnitude. The underlying reason is based on the increase in the reducing capacity of the Tc-containing spinels upon doping. This can be quantified by the difference in energy between the Fermi level,  $E_F$ , and the highest occupied Tc  $d$  states,  $\Delta E_{gap}$ , see last column in Table 1. The calculated total density of states and projected density of states of  $d$ -band for Tc and dopant are shown in Supplementary Fig. 6. Whereas in the case of Ni, only a marginal stabilization of the Tc  $d$ -states occurs (small  $\Delta E_{gap}$ ), in the case of Zn and Co, a much higher stabilization takes place that ultimately hinders Tc re-oxidation.

## Discussion

In concluding, we propose that standard reduction potentials of transition metal ions relative to those of parent spinel, combined with their available oxidation states, can be a useful diagnostic tool for identifying appropriate additives. The reduction potential for magnetite ranges from +0.22 to +0.66 V<sup>33</sup> while those for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  are -0.28, -0.26, -0.76 V, respectively,<sup>34</sup> and in principle  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  should have similar and limited effect upon Tc retention, while  $\text{Zn}^{2+}$  should have a more pronounced influence. However,  $\text{Co}^{2+}$  can be further oxidized to  $\text{Co}^{3+}$ , with a strong oxidation potential of -1.82 V, and therefore it greatly increases the reducing capacity of the spinel material.<sup>35</sup> Both simulations and experiment show that Cobalt is by far the most effective additive for Tc retention compared to the undoped magnetite. We postulate that Tc retention, during the glass vitrification, can

1 be controlled by balancing the redox capacity of oxide materials and doping agents.  
2 The current study underscores the impact of complex models incorporating both  
3 electronic structure and temperature effects that reveal the critical variables needed  
4 for predictive materials design.

## 5 **Methods**

### 6 **Density functional theory (DFT) parameters**

7 Spin-polarized DFT simulations were performed with periodic boundary conditions (3D  
8 PBC) as implemented in the CP2K package.<sup>36</sup> The Perdew, Burke and Ernzerhof (PBE)  
9 generalized gradient approximation was used for the exchange-correlation functional.<sup>37</sup> The  
10 core electrons were described by the norm-conserving pseudopotentials,<sup>38</sup> while the  
11 valence wave functions were expanded in terms of double-zeta quality basis sets optimized  
12 for condensed systems to minimize linear dependencies and superposition errors.<sup>39</sup> An  
13 additional auxiliary plane wave basis set with a 500-Ry cutoff was used to calculate the  
14 electrostatic terms. The GGA+U scheme was used to provide more accurate electronic  
15 structure for the localized *d*-orbitals. The Hubbard parameter (U-J) of 3.5 eV was taken for  
16 the Fe 3d states, which results in a work function of 5.32 eV, in good agreement with that  
17 obtained by Pentcheva *et al.*<sup>27</sup> Due to large supercell simulations, the  $\Gamma$ -point  
18 approximation was used for the Brillouin zone integration.

### 19 **Computational models**

20 To study Tc incorporation in magnetite with and without dopants, we used a 2×2×2  
21 supercell in all simulations to minimize periodic images. Optimization of the bulk structure  
22 of magnetite had a cell parameter of 8.391 Å, which agrees well with experimental data  
23 (8.390 Å<sup>40</sup>). Using this optimized cell parameter, we constructed a magnetite(001) surface

model terminated at an octahedral Fe sublattice, since it is known to be the most stable surface structure in magnetite. A more recent surface model was also considered,<sup>41</sup> but found not to have significant impact on the present problem, see SI. Our model system consisted of a symmetric slab with seven octahedral and six tetrahedral Fe sublattices (384 atoms) with a vacuum region of 12.5 Å between slabs. To study Tc incorporation, one surface octahedral Fe was replaced with Tc, followed by structural optimization. We also optimized a structure with one octahedral Fe in the third layer replaced by Tc. For the doping studies, we substituted a surface Fe atom with Co, Ni, or Zn (~1 wt%) at a lattice position close to Tc. In all simulations, we fixed the atomic positions of the four bottom atomic layers.

## AIMD simulations

AIMD simulations were performed with and without Tc at 25 °C and with the dopants Co/Ni/Zn at 600 °C, with the Nosé-Hoover thermostat for NVT ensemble and a time-step of 1.0 fs. Each simulation was equilibrated for at least 20-28 ps, and the last 10-12 ps of the trajectories were used for the analysis. Due to the big computational cost of high temperature simulations, we chose lower range of vitrification temperatures (600 °C), while experiments were performed at somewhat higher temperatures (~700 °C).

## Spinel synthesis and XAFS analysis

Ni, Zn, or Co-doped Tc-incorporated magnetite was synthesized at high pH (>13). Three solutions of 0.05M Ni, Zn and Co in distilled deionized water (DDI) were prepared using analytical-grade NiCl<sub>2</sub>, ZnCl<sub>2</sub>, and CoCl<sub>2</sub>. Technetium solution (0.001M) was prepared by spiking 10,000 ppm NaTcO<sub>4</sub> stock solution into 1 M NaOH solution. 0.09 g synthesized

1 Fe(OH)<sub>2</sub> dry powder was mixed with 5 mL of NiCl<sub>2</sub>, ZnCl<sub>2</sub>, or CoCl<sub>2</sub> solution in 20-mL poly  
2 vials and shaken on an orbital shaker (120 RPM) for 24 h at room temperature (RT). After  
3 24 h shaking, 15 mL of the Tc-spiked 1 M NaOH was added to each vial and heated in an  
4 oven at 75 °C for 72 h. After cooling to RT, the precipitates were separated using 0.45 µm  
5 filters and washed using ~120 mL DDI water immediately after filtering. The collected solid  
6 precipitates were air-dried at RT overnight and stored in glass vials. Strong microwave-  
7 assisted digestion with a solution consisting of 16 M HNO<sub>3</sub> (17%), 12 M HCl (7%), 32 M HF  
8 (3.3%), 0.5 g H<sub>3</sub>BO<sub>3</sub> (1.5%), and DDI water (71.2%) on a volume basis was used to  
9 determine the total Tc concentration in the final solid samples. For the 600 °C XANES  
10 sample, ~5 g of Tc-magnetite was mixed with other basic glass feeds in a Pt crucible and  
11 heated in a furnace to 1,000 °C at 5 °C increase per minute. After air quenching, the final  
12 glass was pulverized and used for XANES analysis. Additional Tc XAFS samples were also  
13 prepared for Ni, Zn, or Co-doped Tc-incorporated magnetite at room temperature without  
14 basic glass feeds and treated at 700 °C inside an oven. The XAFS spectra were collected at  
15 room temperature on Beamline 4-1 at the Stanford Synchrotron Radiation Laboratory. A  
16 Si(220) double-flat crystal monochromator was used, and the energy was calibrated by  
17 using the first inflection point of the Tc K edge spectrum of the Tc(VII) standard (KTcO<sub>4</sub>)  
18 defined as 21.044 keV. The XAFS spectra of Tc-standards and Tc-magnetite samples were  
19 collected in transmission and fluorescence mode, respectively, at RT using a 13-element  
20 germanium detector. Data reduction and analysis were performed using the software  
21 IFEFFIT and Athena/Artemis<sup>42</sup> after detector dead-time correction. The XANES spectra for  
22 Tc samples were fit using a linear combination of the XANES spectra of KTcO<sub>4</sub> as the Tc(VII)  
23 standard spectrum and TcO<sub>2</sub>•2H<sub>2</sub>O as the Tc(IV) standard spectrum, see Supplementary Fig.  
24 7 and Supplementary Methods for more details.<sup>31</sup>

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## 16   **Author Contributions**

17   All authors provided input for the manuscript. M. L. contributed to the planning and  
18   executed the simulations and analyzed the data, W. U., G. W. and W. L. performed the  
19   experiments and related data analysis. R.R. provided pseudopotentials for the  
20   calculations and contributed to the analysis of the data. V.-A. G planned and

1 supervised the research. M. L., R. R., and V.-A. G. jointly wrote the manuscript with  
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### 6 **Competing financial interests**

7 The authors declare no competing financial interests.

### 8 **Supplementary information**

9

10 PDF files

11

12 1. Supplementary Information

13 Supplementary Figures 1-7 and Supplementary Tables 1-4

14 Supplementary movies

15 1. Supplementary Movie 1

16 The movie is generated from AIMD simulations at 600 °C showing leaching of  
17 Tc out of the magnetite surface, forming a tetrahedral (TcO<sub>4</sub>)<sup>-</sup>.

18 2. Supplementary Movie 2

19 The movie is generated from AIMD simulations at 600 °C showing (TcO<sub>4</sub>)<sup>-</sup>  
20 returning into the magnetite surface, in the presence of Co dopant.

21

**Figure 1| The B-truncated (octahedral Fe) Fe<sub>3</sub>O<sub>4</sub>(001) structure.**

(a) Top view and (b) side view of surface structure. Red and cyan circles represent oxygen and iron, respectively. A (blue circle) can be either Fe or Tc and B (yellow circle) can be either Fe or an impurity atom (Ni/Zn/Co).

**Figure 2| Structural properties and XANES spectra in the presence of Tc.**

(a) Atomic density profile showing atomic arrangement along z-direction at 25 and 600°C obtained from AIMD simulations, where dotted vertical line denotes the magnetite surface. (b) Pair distribution function g(R) obtained from AIMD simulation trajectories at 25 and 600°C. (c) Snapshot of the structure at 600°C from AIMD trajectories where a blue circle represents Tc, red for O, and cyan for Fe. The dotted vertical line denotes the magnetite surface. (d) Normalized XANES spectra at 25 and 600°C.

**Figure 3| Atomic density and normalized XANES spectra with Co dopant.**

(a) Atomic density profiles with and without Co dopant at 600 °C. Red lines represent Tc, blue line for doped atom, gray lines for Fe, and green lines for O. (b) Normalized XANES spectra for the Co doped magnetite at 25 °C as made and treated at 700 °C. Color codes used are the same as those shown in Fig. 2

1 **Table 1|** Equilibrium constants and free energy estimates considering doping effects. Tc implies  
2 system without dopant. Relative populations determined as a ratio from the computed  $K_{eq}$  values.  
3 Experimental values correspond to the amount of Tc remaining in the doped magnetite after  
4 exposure to 700 °C.  $\Delta E_{gap}$  represents the energy difference between the Fermi level  $E_F$  and the  
5 Tc HOMO energy from the total projected DOS.

Doping	$K_{eq}$	$\Delta G$ (kJ mol <sup>-1</sup> )	Exp. Retention (%wt)	$\Delta E_{gap}$ (eV)
Tc	0.15	14.2	--	0.15
Tc/Ni	0.56	4.3	4	0.35
Tc/Zn	2.79	-7.7	12	1.03
Tc/Co	21.80	-23.1	29	1.12

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